

## Partial Translation of D1 (JP H07-321444 A)

Page 2, paragraph [0001]

Field of Utilization in Industry

This invention relates to a process for forming a metal pattern. More particularly, it relates to a process for forming a metal pattern which comprises selectively forming a metal wiring on a surface of an insulating resin film for making a thin film multilayer circuit board and others.

Pages 3-4, paragraphs [0016] to [0022]

In Fig. 1(a), a fine Cu particles-containing layer 2 is formed from a dispersion of fine Cu particles having average particle diameter of about 2  $\mu\text{m}$  on an insulating resin film composed of polyimide resin, an olefin resin or others. The insulating resin layer 2 is formed on a substrate board such as silicon wafer (although not shown in the figure). The substrate board on which the insulating resin layer is formed may be either an insulating substrate board made of ceramics, mica, glass, aluminum nitride (AlN) or the like, or a conductive substrate board made of aluminum or others. ... (partially omitted) ...

In Fig. 1(b), the fine Cu particles-containing layer 2 is dried. ... (partially omitted) ... whereby the solvent in the fine Cu particles-containing layer 2 is evaporated to form a solid fine Cu particles layer 3.

As shown in Fig. 1(c), the surface of the fine Cu particles layer 3 is irradiated with excimer laser through a metal mask 4 made of stainless steel, whereby the fine Cu particles in the layer 3 are selectively melted. ... (partially omitted) ...

Finally, as shown in Fig. 1(d), the substrate board having the selectively laser-irradiated fine Cu particles layer is immersed in an organic solvent 6 such as acetone or ethanol in a vessel 7, and the vessel is gently shaken. ... (partially omitted) ...

Cu particles in a region other than molten Cu region 3a are removed by the organic solvent 6, and consequently, a Cu wiring layer is formed from molten Cu region 3a on the surface of the insulating resin thin film 1. ... (partially omitted) ...

Further, an insulating resin thin film can be formed on the thus-formed Cu wiring layer, and a Cu wiring layer is formed on the an insulating resin thin film. By repeating this procedure, a thin film multilayer circuit board can be made.

Pages 4-5, paragraphs [0024] to [0029]

In Fig. 1(a), a surface of an insulating resin thin film 11 is irradiated with excimer laser 13 through a metal mask 12 made of stainless steel and having a wiring pattern formed thereon. The insulating resin thin film 11 is formed on a substrate board such as silicon wafer (although not shown in the figure). The substrate board may be either an insulating substrate board made of ceramics, mica, glass, aluminum nitride (AlN) or the like, or a conductive substrate board made of aluminum or others. As the laser 13, KrF excimer laser with wavelength 248 nm is used. ... (partially omitted) ...

In Fig. 2(b), the insulating resin thin film 11 selectively irradiated with laser is washed with acetone 10, and then immersed in a solution 14 of silver trifluoroacetate. ... (partially omitted) ..., whereby a single atom layer of Ag atom is formed on the insulating resin thin film 11.

... (partially omitted) ... The single Ag atom layer 15 is formed on a laser 13-irradiated region of the insulating resin thin film 11. Obviously the single Ag atom layer 15 is electrically conductive.

In Fig. 2(c), a Cu wiring layer 16 is formed on the single Ag atom layer 15 on the insulating resin thin film 11. ... (partially omitted) ...

Further, an insulating resin thin film can be formed on

the thus-formed Cu wiring layer, and a Cu wiring layer is formed on the an insulating resin thin film. By repeating this procedure, a thin film multilayer circuit board can easily be made.

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-321444

(43)Date of publication of application : 08.12.1995

(51)Int.Cl.

H05K 3/10  
G23C 26/00  
H01L 21/268  
H05K 3/02  
H05K 3/46

(21)Application number : 06-109924

(71)Applicant : FUJITSU LTD

(22)Date of filing : 24.05.1994

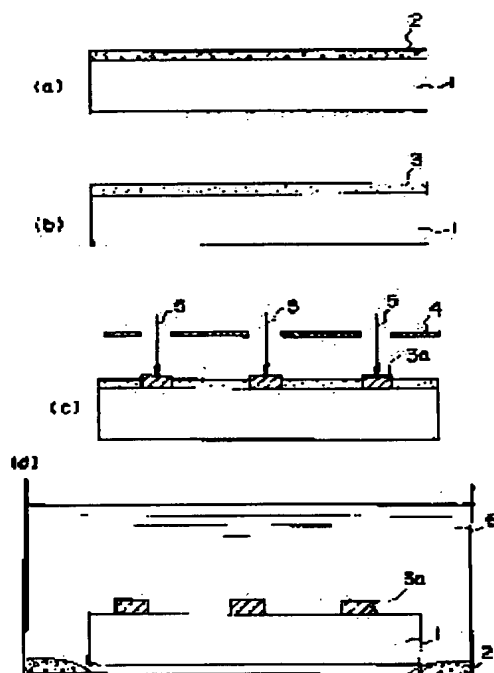
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## (54) METAL PATTERN FORMING METHOD

### (57)Abstract:

**PURPOSE:** To simplify forming process and to improve throughput in a method for forming a metal pattern for forming wiring selectively on an insulation resin layer surface for constituting a thin-film multilayer circuit board, etc.

**CONSTITUTION:** The title method includes a process for forming a metal fine particle layer 2 on the surface of an insulation resin layer 1, a process for melting the metal fine particle layer 2 located at a desired region by applying laser beams to a specific region on the surface of the metal fine particle layer 2, and a process for eliminating the metal fine particle layer 2 which is not melted by applying laser beams from the surface of the insulation resin layer 1.



## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

- [Claim 1] The metal pattern-formation approach characterized by to have the process which forms a metal particle layer (2) in the front face of an insulating resin layer (1), the process which irradiate laser to the request field of said metal particle layer (2) front face, and fuse said metal particle layer (2) in this request field, and the process which remove said metal particle layer (2) which did not fuse by the exposure of said laser from said insulating resin layer (1) front face.
- [Claim 2] Said metal particle layer (2) is the metal pattern formation approach according to claim 1 characterized by being the paste ingredient which consists of mixture of a metal particle and an organic solvent, and forming said metal particle layer (2) by carrying out skiing JINGU of this paste ingredient.
- [Claim 3] The metal pattern formation approach according to claim 2 characterized by heating said metal particle layer (2) and removing said organic solvent before irradiating said laser on said metal particle layer (2) front face.
- [Claim 4] Said laser is the metal pattern formation approach according to claim 1 characterized by irradiating in the ambient atmosphere of inert gas.
- [Claim 5] Said metal particle layer (2) which was not fused with said laser is the metal pattern formation approach according to claim 1 characterized by being removed using an organic solvent.
- [Claim 6] The beam of light of predetermined energy is irradiated to the request field of the front face of insulating resin (11). The process which reforms the request field of said insulating resin (11) front face, and the process which a metal atom is made to adhere to the field to which reforming of said insulating resin (11) front face was carried out, and forms a thin metal atomic layer (15) in it. The metal pattern formation approach characterized by having the process which forms a metal wiring layer (16) by using said metal atomic layer (15) as a foundation.
- [Claim 7] Said insulating resin (11) is the metal pattern formation approach according to claim 6 which is polyimide resin or olefine resin and is characterized by a carboxyl group arising on said insulating resin (11) front face by irradiating the beam of light of said predetermined energy.
- [Claim 8] The metal pattern formation approach according to claim 7 characterized by transposing the hydrogen atom of said carboxyl group to a metal atom in order to make a metal atom adhere to the field to which reforming of said insulating resin (11) front face was carried out.
- [Claim 9] Said metal atom is the metal pattern formation approach according to claim 6 characterized by being silver.
- [Claim 10] Said metal wiring layer (16) is the metal pattern formation approach according to claim 6 characterized by being formed of the electrolytic plating which uses said metal atomic layer (15) as an electrode.
- [Claim 11] The metal pattern formation approach according to claim 6 characterized by using the beam of light whose wavelength is 180nm - 250nm as a beam of light which reforms the request field of said insulating resin (16) front face.

[Translation done.]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] About the metal pattern formation approach, in more detail, since a thin film multilayered circuit board etc. is constituted, this invention relates to the metal pattern formation approach which forms wiring in an insulating resin front face alternatively.

[0002]

[Description of the Prior Art] In recent years, in order to carry out densification of the wiring in the circuit board used for a large-sized computer etc., the thin film multilayered circuit board which carried out the laminating of a thin film insulation resin layer and wiring layers, such as polyimide, by turns, and formed them is in use. The process of formation of an insulating layer and a wiring layer is repeated as the beer hole for forming a thin film insulation resin layer for example, on a silicon wafer, and taking the flow between layers is opened, and it forms a circuit pattern in the front face alternatively, and a thin film insulation resin layer is formed again and a circuit pattern is formed on it again, in order to constitute such a thin film multilayered circuit board.

[0003] In order to form a circuit pattern in a thin film insulation resin front face conventionally, the lift-off method was used in many cases. In order to form a circuit pattern by the lift-off method, for example, the spin coat of the resist which has photosensitivity is carried out, the metal mask after baking and corresponding to a circuit pattern is first, minded on an insulating resin layer, and a resist is exposed and developed. Next, a wiring metal is made to adhere all over a resist top by a spatter etc. Then, using a solvent, it exfoliates together with a resist and the wiring metal of a unnecessary part is removed. Thereby, on an insulating resin layer, only a metal part required for wiring is left behind and a circuit pattern is formed.

[0004]

[Problem(s) to be Solved by the Invention] However, by such formation approach of the conventional wiring, in order to form wiring, much time amount is required, and there was a problem that the throughput of wiring formation was low. For example, by the lift-off method, resist spreading, a \*\*\*-king, exposure and development, a spatter, resist exfoliation, etc. need many processes relevant to a resist by the time it forms a circuit pattern on an insulating resin layer.

[0005] Moreover, in order to form wiring alternatively on an insulating resin layer, if the lift-off method is used, the wiring metal of the unnecessary part of the wiring metal layers once formed all over the resist top will be removed, but since a resist is also removed together with a unnecessary wiring metal at this time, to the removed unnecessary wiring metal, a resist can be mixed, and cannot reuse, but a wiring metallic material becomes useless. By the futility of this wiring metal, the problem of raising the cost of a thin film multilayered circuit board as a result arises.

[0006] This invention is made in view of such a problem, and it aims at simplifying a formation process and raising a throughput in the metal pattern formation approach which forms wiring in an insulating resin layer front face alternatively.

[0007]

[Means for Solving the Problem] The process which forms the metal particle layer 2 in the front face of the insulating resin layer 1 so that the above-mentioned technical problem may be illustrated to drawing 1. The process which irradiates laser to the request field of said metal particle layer 2 front face, and fuses said metal particle layer 2 in this request field, it solves by the metal pattern formation approach characterized by having the process which removes said metal particle layer 2 which was not fused by the exposure of said laser from said insulating resin layer 1 front face.

[0008] Said metal particle layer 2 is a paste ingredient which consists of mixture of a metal particle and an organic solvent, and solves said metal particle layer 2 by the metal pattern formation approach characterized by being formed by carrying out skiing JINGU of this paste ingredient. Before irradiating said laser on said metal particle layer 2 front face, it solves by the metal pattern formation approach characterized by heating said metal particle layer 2 and removing said organic solvent.

[0009] Said laser is solved by the metal pattern formation approach characterized by irradiating in the ambient atmosphere of inert gas. Said metal particle layer 2 which was not fused with said laser is solved by the metal pattern formation approach characterized by being removed using an organic solvent. Or the beam of light of predetermined energy is irradiated to the request field of the front face of insulating resin 11 so that it may illustrate to drawing 2. The process which reforms the request field of said insulating resin 11 front face, and the process which a metal atom is made to adhere to the field to which reforming of said insulating resin 11 front face was carried out, and forms the thin metal atomic layer 15 in it, it solves by the metal pattern formation approach characterized by having the process which forms the metal wiring layer 16 by using said metal atomic layer 15 as a foundation.

[0010] It solves by the metal pattern formation approach which said insulating resin 11 is polyimide resin or olefine resin, and is characterized by a carboxyl group arising on said insulating resin 11 front face by irradiating the beam of light of said predetermined energy. In order to make a metal atom adhere to the field to which reforming of said insulating resin 11 front face was carried out, it solves by the metal pattern formation approach characterized by transposing the hydrogen atom of said carboxyl group to a metal atom.

[0011] Said metal atom is solved by the metal pattern formation approach characterized by being silver. Said metal wiring layer 16 is solved by the metal pattern formation approach characterized by being formed of the electrolytic plating which uses said metal atomic layer 15 as an electrode. As a beam of light which reforms the request field of said insulating resin 16 front face, wavelength is solved by the metal pattern formation approach characterized by using the beam of light which is 180nm - 250nm.

[0012]

[work ---] for According to this invention, after applying to the front face of an insulating resin layer the paste-like ingredient which mixed the metal particle with the organic solvent by skiing JINGU etc., forming a metal particle layer in it and then carrying out heating removal of the organic solvent in a paste-like ingredient, laser is irradiated to the circuit pattern formation field of an insulating resin layer front face through the metal mask of a circuit pattern. Thereby, a metal particle fuses and is united and adheres to an insulating resin layer front face. If laser radiation is performed in an inert gas ambient atmosphere, it can fuse without oxidizing a metal particle and making it deteriorate. And the unnecessary metal particle which an insulating resin front face did not fuse is removed using an organic solvent. The metal layer of the field which irradiated laser remains in an insulating resin layer front face by this, and a circuit pattern is formed.

[0013] Therefore, the metal pattern formation approach can be made to simplify compared with the lift-off method etc. Moreover, the unnecessary metal particle removed from the insulating resin layer front face is reusable. Moreover, as an option, the beam of light of predetermined energy, such as laser, is irradiated through the metal mask of a circuit pattern to the circuit pattern formation field of the front face of insulating resin layers, such as polyimide resin and olefine resin, and an insulating resin layer front face is reformed so that a metal atom may adhere. The benzene ring in resin breaks by the exposure of the beam of light of predetermined

energy (opening and closing), and reforming of this is carried out so that a carboxyl group may arise on a resin front face. Next, for example, with a silver tri-fluoroacetate solution, metal atoms, such as Ag, are made to adhere to a monoatomic layer, and a metal atomic layer is formed in the field to which reforming of the insulating resin front face was carried out. Electrolytic plating is carried out by using this metal atomic layer as an electrode, and a wiring metal layer is formed on a metal atomic layer.

[0014] Thereby, the metal pattern formation approach can be made to simplify compared with the lift-off method etc. Moreover, since a wiring metal can be made to adhere only to the wiring formation field of an insulating resin substrate, futility which removes and discards a unnecessary wiring metal is avoidable.

[0015]

[Example] Then, the example of this invention is explained based on a drawing below.

(The 1st example) drawing 1 (a) - drawing 1 (d) Each process of the metal pattern formation approach concerning the 1st example of this invention is shown roughly.

[0016] drawing 1 (a) \*\*\*\* — Cu particle content layer 2 which mixed Cu particle (copper particle) with a mean particle diameter of about 2 micrometers to solvents, such as an acetone, is formed at 10 micrometers in thickness on the insulating resin thin film 1 which consists of polyimide resin, olefine resin, etc. In fact, although this insulating resin thin film 1 is formed on substrates, such as a silicon wafer which is not illustrated, it is omitted in this drawing.

Conductive substrates, such as insulating substrates, such as a ceramic, a mica, glass, and nitriding aluminum (AlN), or aluminum, are sufficient as the substrate which forms this insulating resin thin film 1. Moreover, the ingredient of the metal particle of Cu particle content layer 2 may have a desirable metal with the low melting point with high and conductivity, and aluminum etc. is sufficient as it. By carrying out skin JINGU of what mixed Cu particle and the solvent and was made into the shape of a paste on insulating resin thin film 1 front face, Cu particle content layer 2 is easy, and can do \*\* applied to homogeneity.

[0017] Next, drawing 1 (b) Cu particle content layer 2 is then dried. At this process, it is drawing 1 (a). The substrate in which shown Cu particle content layer 2 was formed is put into the oven of nitrogen-gas-atmosphere mind that Cu does not oxidize, and it dries for 10 minutes at 60 degrees C. Thereby, the solvent in Cu particle content layer 2 evaporates, and only Cu particle remains and becomes Cu particle layer 3 in the condition of having solidified.

[0018] Next, drawing 1 (c) Excimer laser 5 is irradiated on Cu particle layer 3 front face through the metal mask 4 which consists of stainless steel, and melting of the Cu particle in Cu particle layer 3 is alternatively carried out so that it may be shown. The circuit pattern which forms the metal mask 4 on the insulating resin thin film 1 is minced. Laser 5 irradiates KrF excimer laser with a wavelength of 248nm by ten pulses in energy density 1.0 J/cm<sup>2</sup> and 150ns of irradiation time. At this time, argon gas inactive as a controlled atmosphere is used so that Cu may not oxidize.

[0019] Thereby, the field where the laser 5 of Cu particle layer 3 was irradiated goes up in temperature of about 1000 degrees C, and Cu particle fuses, respectively, and it unifies and adheres to insulating resin thin film 1 front face as melting Cu field 3a. Moreover, since the field where laser 5 was not irradiated among Cu particle layers 3 is not fused, Cu particle continues being in the scattering condition separated, respectively.

[0020] It is drawing 1 (d) to the last. The substrate which carried out laser radiation then alternatively in Cu particle layer 3 is dipped in the organic solvents 6, such as an acetone in a container 7, and ethanol, and is stirred lightly. As this organic solvent 6, what does not oxidize metal particles, such as Cu, is desirable. Thereby, it dissociates from insulating resin thin film 1 front face, and all Cu particles other than melting Cu field 3a of Cu particle layer 3 are mixed with an organic solvent 6, and precipitate to the direction under a container 7 after a while.

Since Cu particle of melting Cu field 3a fused and has adhered to insulating resin thin film 1 front face, in an organic solvent 6, it separates and it is not removed.

[0021] In this way, if Cu particle of fields other than melting Cu field 3a is removed from insulating resin thin film 1 front face, as a result, melting Cu field 3a will be left behind to insulating resin thin film 1 front face, and it will be wiring on it. In this example, with a width-of-

face thickness [ 5-micrometer thickness of 10 micrometers ] wiring was formed. Thus, by applying to an insulating resin thin film front face the paste which mixed Cu particle with the organic solvent, and irradiating laser alternatively through the metal mask of a circuit pattern at the paste layer, Cu particle of a laser radiation field fuses and it adheres to an insulating resin thin film front face. Then, by dipping this substrate into an organic solvent, unnecessary Cu particle of the field by which laser radiation was not carried out is separated into an organic solvent, only fused Cu layer remains in an insulating resin thin film front face, and wiring is formed.

[0022] An insulating resin thin film can be formed on the wiring layer formed here, wiring can be formed by approach which was explained above on it, and a thin film multilayered circuit board can be formed by repeating it. Therefore, since a long process like the lift-off method is not needed, wiring formation is simplified and the throughput of wiring formation improves.

[0023] Moreover, unnecessary Cu particle separated from the insulating resin thin film front face with the organic solvent is reusable in the condition of having dissociated from the organic solvent or having been mixed with the organic solvent, and the futility of a wiring metal can decrease sharply and it can reduce the manufacturing cost of a thin film multilayered circuit board.

(The 2nd example) Drawing 2 (a) - (c) Each process of the wiring formation approach concerning the 2nd example of this invention is shown roughly.

[0024] Drawing 2 (a) Laser 13 is irradiated through the metal mask 12 which consists of stainless steel with which the circuit pattern was then formed in the front face of the insulating resin thin film 11, such as polyimide resin and olefine resin. In fact, the insulating resin thin film 11 is omitted here, although formed on substrates, such as a silicon wafer. Moreover, as this substrate, conductive substrates, such as insulating substrates, such as a ceramic, a mica, glass, and nitriding aluminum (AlN), or aluminum, may be used again. KrF excimer laser with a wavelength of 248nm is used for laser 13, it is energy density 100 mJ/cm<sup>2</sup> and 15ns (one pulse) of irradiation time, and is atmospheric air. It irradiates in an ambient atmosphere. Thus, by irradiating laser 13 to the circuit pattern formation field of the insulating resin thin film 11, the benzene ring contained in polyimide resin, olefine resin, etc., of insulating resin thin film 11 front face breaks (opening and closing), and a carboxyl group (-COOH) arises on insulating resin thin film 11 front face. The depth of this open chain is about 3000A from insulating resin thin film 11 front face, and a carboxyl group is produced so that it may appear in the front-face side of the insulating resin thin film 11. Thus, in order for the front face of the insulating resin thin film 11 to reform, the wavelength of laser 13, irradiation time, and the conditions of energy density must be suitable. Wavelength needs to be contained in the absorption band of the resin currently used for the insulating resin thin film 11, its range of 180nm - 250nm is desirable here, and its ArF excimer laser (wavelength of 193nm) is specifically more desirable. moreover — since the insulating resin thin film 11 will evaporate if energy density is too high — energy density — 40 mJ/cm<sup>2</sup> (threshold) - 100 mJ/cm<sup>2</sup> — it is better to hold down to a certain amount of height. Irradiation time is decided by the amount of energy related to the wavelength and energy density of laser 13.

[0025] drawing 2 (b) \*\*\*\* — the insulating resin thin film 11 by which laser radiation was carried out alternatively is \*\*\*\*(ed) for 10 minutes after washing with an acetone 10 in the silver tri-fluoroacetate (CF<sub>3</sub>COOAg) solution 14 of 10-2M. The following chemical reactions progress by this, the hydrogen atom of a being [ it / in an insulating resin thin film 11 front-face side ] carboxyl group and Ag atom of silver tri-fluoroacetate 14 permute, and the monoatomic layer of Ag atom is formed in insulating resin thin film 11 front face.

[0026]

- COOH+CF<sub>3</sub>COOAg -> -COOAg Since a carboxyl group is produced in the front-face side of the insulating resin thin film 11 as mentioned above although the +CF<sub>3</sub>COOAg atom is combined in fact as some organic compounds which constitute polyimide resin and olefine resin, Ag atom is also arranged only on the front face of the insulating resin thin film 11, and the Ag atomic layer 5 is formed. Since this carboxyl group is produced only to the field to which the laser 13 of insulating resin thin film 11 front face was irradiated, this Ag atomic layer 15 is



formed only in the field to which laser 13 was irradiated. Moreover, this Ag atomic layer 15 has conductivity clearly.

[0027] Drawing 2 (c) The Cu wiring layer 16 is formed as a circuit pattern on the Ag atomic layer 15 of insulating resin thin film 11 front face. This puts in the insulating resin thin film 11 into a copper-sulfate solution (not shown), performs electrolytic plating by using the Ag atomic layer 15 as an electrode, and is performed by growing up the Cu wiring layer 16 only into a field with the Ag atomic layer 15. In this example, the Cu wiring layer 16 with a width of face [of 10 micrometers] and a thickness of 5 micrometers was formed.

[0028] Thus, the laser 13 which has predetermined energy through the metal mask 12 of a circuit pattern on the front face of the insulating resin thin film 11 is irradiated, and insulating resin thin film 11 front face is reformed alternatively. And the Ag atomic layer 15 can be formed in the part by which reforming was carried out with a silver tri-fluoroacetate solution, and a circuit pattern can be formed for the Cu wiring layer 16 on the insulating resin thin film 11 by formation \*\*\*\*\* as an electrode with electrolytic plating using the Ag atomic layer 15.

[0029] Therefore, in the approach of forming a circuit pattern, since a twist can also simplify a process by the lift-off method, the throughput of wiring formation improves. Moreover, since it adheres to a wiring metal alternatively only to the circuit pattern formation field of insulating resin thin film 11 front face, the futility of a wiring metal is lost and the cost of wiring formation is reduced. Moreover, on the circuit pattern formed in this example, the laminating of the insulating resin thin film is carried out further, and a circuit pattern is formed by the approach that it is the same on it. By repeating this, a thin film circuit substrate can be formed easily. (The 3rd example) Next, the wiring formation approach concerning the 3rd example of this invention is explained.

[0030] the 2nd example and principle target which explained this example previously — the same — drawing 2 (a) — drawing 2 (c) The process and flow which were explained are the same.

Different points from the 2nd example are 2 Figs. (a) at the 2nd example. Although excimer laser was used in order to reform alternatively insulating resin thin film 11 front face in a process, in this example, it is the point which uses a mercury lamp.

[0031] Ultraviolet rays with a wavelength [by the mercury lamp] of 185nm are irradiated in energy density 20 mJ/cm<sup>2</sup>, irradiation time 100min, and the reduced pressure ambient atmosphere of 10 to 3 or less Torr. If a mercury lamp is used, since irradiation time will become [energy density] lower than the case where laser is used, for a long time, it is necessary to make an ambient atmosphere into a vacuum so that an exposure part may not be influenced of surrounding oxygen.

[0032] After reforming the request field of an insulating resin thin film front face, Ag atomic layer is formed in the field by which reforming was carried out with a silver tri-fluoroacetate water solution like the 2nd example, on the Ag atomic layer, a wiring metal layer is grown up and a circuit pattern is formed. Moreover, also in this example, the same operation and effectiveness as the 2nd example are acquired.

[0033]

[Effect of the Invention] As stated above, if laser is irradiated to the field which applies the paste containing metal particles, such as Cu, and forms the circuit pattern of the paste layer on the insulating resin thin film formed on the substrate according to this invention, the metal particle of a laser radiation field will fuse and it will adhere to an insulating resin thin film front face, and the metal particle of the field which was not fused by laser radiation is removed by the organic solvent. Thereby, compared with the lift-off method etc., a wiring formation process is simplified and the throughput of wiring formation can be raised. Moreover, since the unnecessary metal particle removed from the insulating resin thin film front face is easy to collect and it can reuse it, it can reduce the cost of wiring formation.

[0034] Moreover, according to the option of this invention, irradiate the beam of light of predetermined energy to the circuit pattern formation field of the insulating resin thin film front face formed on the substrate, reform a front face, a very thin metal atomic layer is made to form in that reforming field, and a wiring metal layer is formed by using this metal atomic layer as a foundation. Also in this approach, the process for forming wiring is simplified by this compared

with the lift-off method etc., and the throughput of wiring formation can be raised. Furthermore, since an insulating resin thin film front face adheres only to a metallic material required in order to form wiring, and a wiring metallic material is removed from an insulating resin thin film front face and discarded like the lift-off method, the futility of a wiring metallic material is lost and cost of wiring formation can be made low.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The wiring formation approach concerning the 1st example of this invention is shown, and it is (a). - (d) It is drawing showing each of that process.

[Drawing 2] The wiring formation approach concerning the 2nd example of this invention is shown, and it is (a). - (c) It is drawing showing each of that process.

[Description of Notations]

- 1 11 Insulating resin thin film
- 2 Cu Particle Content Layer
- 3 Cu Particle Layer
- 3a Melting Cu layer
- 4 12 Metal mask
- 5 13 Laser
- 6 Organic Solvent
- 7 Container
- 14 Silver Tri-fluoroacetate Solution
- 15 Ag Atomic Layer
- 16 Cu Wiring Layer

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[Translation done.]

# METAL PATTERN FORMING METHOD

Publication number: JP7321444

Publication date: 1995-12-08

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Applicant: FUJITSU LTD

Classification:

- International: C23C26/00; H01L21/268; H01L21/302; H05K3/02; H05K3/10; H05K3/46; C23C26/00; H01L21/02; H05K3/02; H05K3/10; H05K3/46; (IPC1-7): H05K3/10; C23C26/00; H01L21/268; H05K3/02; H05K3/46

- European:

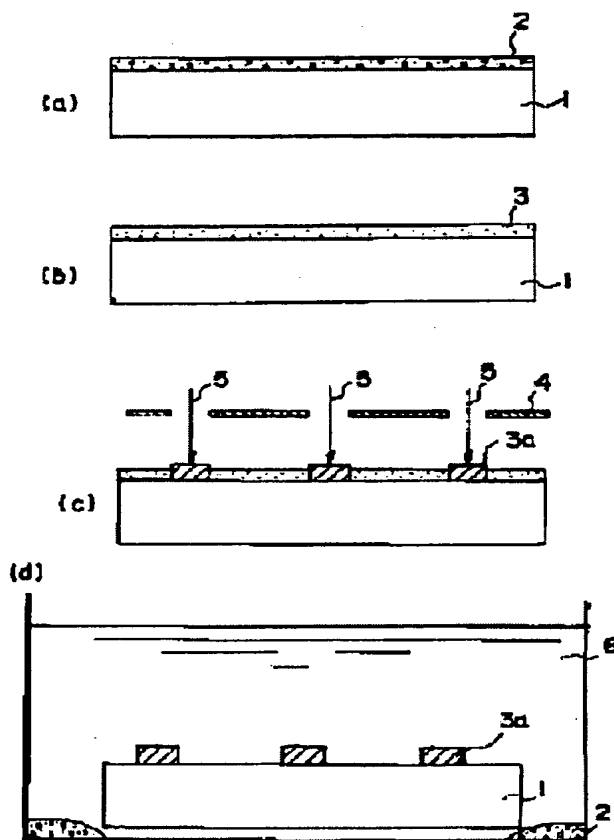
Application number: JP19940109924 19940524

Priority number(s): JP19940109924 19940524

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## Abstract of JP7321444

**PURPOSE:** To simplify forming process and to improve throughput in a method for forming a metal pattern for forming wiring selectively on an insulation resin layer surface for constituting a thin-film multilayer circuit board, etc. **CONSTITUTION:** The title method includes a process for forming a metal fine particle layer 2 on the surface of an insulation resin layer 1, a process for melting the metal fine particle layer 2 located at a desired region by applying laser beams to a specific region on the surface of the metal fine particle layer 2, and a process for eliminating the metal fine particle layer 2 which is not melted by applying laser beams from the surface of the insulation resin layer 1.



(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平7-321444

(43) 公開日 平成7年(1995)12月8日

| (51) Int.Cl. <sup>6</sup> | 識別記号 | 序内整理番号  | F I | 技術表示箇所 |
|---------------------------|------|---------|-----|--------|
| H 0 5 K 3/10              | B    | 7511-4E |     |        |
| C 2 3 C 26/00             | E    |         |     |        |
| H 0 1 L 21/268            | Z    |         |     |        |
| H 0 5 K 3/02              | Z    |         |     |        |
| 3/46                      | B    | 6921-4E |     |        |

審査請求 未請求 請求項の数11 O L (全 6 頁) 最終頁に続く

(21) 出願番号 特願平6-109924

(22) 出願日 平成6年(1994)5月24日

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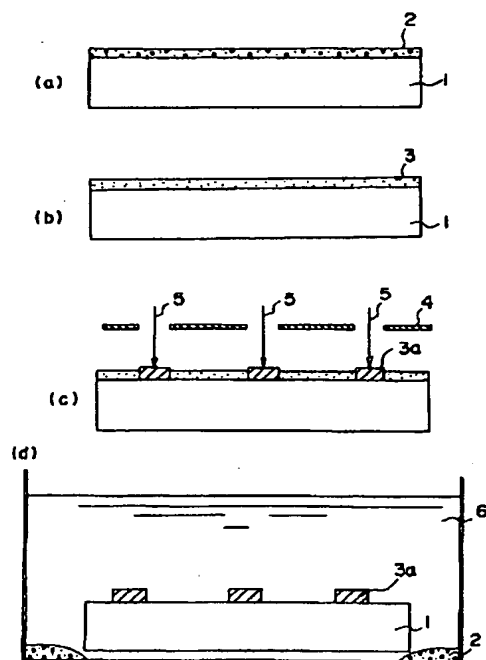
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(54) 【発明の名称】 金属パターン形成方法

(57) 【要約】

【目的】 薄膜多層回路基板などを構成するために絶縁性樹脂表面に配線を選択的に形成する金属パターン形成方法に関し、絶縁性樹脂層表面に選択的に配線を形成する金属パターン形成方法において、形成工程を簡略化してスルーボットを高めること。

【構成】 絶縁性樹脂層1の表面に金属微粒子層2を形成する工程と、前記金属微粒子層2表面の所望領域にレーザを照射して、該所望領域にある前記金属微粒子層2を溶融する工程と、前記絶縁性樹脂層1表面から前記レーザの照射により溶融しなかった前記金属微粒子層2を除去する工程とを含む。



## 【特許請求の範囲】

【請求項1】 絶縁性樹脂層(1)の表面に金属微粒子層(2)を形成する工程と、

前記金属微粒子層(2)表面の所望領域にレーザを照射して、該所望領域にある前記金属微粒子層(2)を溶解する工程と、

前記絶縁性樹脂層(1)表面から前記レーザの照射により溶解しなかった前記金属微粒子層(2)を除去する工程とを有することを特徴とする金属パターン形成方法。

【請求項2】 前記金属微粒子層(2)は、金属微粒子と有機溶媒の混合物からなるペースト材料であり、前記金属微粒子層(2)は該ペースト材料をスキージングすることにより形成されることを特徴とする請求項1記載の金属パターン形成方法。

【請求項3】 前記金属微粒子層(2)表面に前記レーザを照射する前に、前記金属微粒子層(2)を加熱して前記有機溶媒を取り除くことを特徴とする請求項2記載の金属パターン形成方法。

【請求項4】 前記レーザは、不活性ガスの雰囲気中で照射されることを特徴とする請求項1記載の金属パターン形成方法。

【請求項5】 前記レーザにより溶解しなかった前記金属微粒子層(2)は有機溶媒を用いて除去されることを特徴とする請求項1記載の金属パターン形成方法。

【請求項6】 絶縁性樹脂(11)の表面の所望領域に所定エネルギーの光線を照射して、前記絶縁性樹脂(11)表面の所望領域を改質する工程と、

前記絶縁性樹脂(11)表面の改質された領域に金属原子を付着させて、薄い金属原子層(15)を形成する工程と、

前記金属原子層(15)を土台として金属配線層(16)を形成する工程とを有することを特徴とする金属パターン形成方法。

【請求項7】 前記絶縁性樹脂(11)はポリイミド樹脂またはオレフィン樹脂であり、前記所定エネルギーの光線を照射することにより前記絶縁性樹脂(11)表面にカルボキシル基が生じることを特徴とする請求項6記載の金属パターン形成方法。

【請求項8】 前記絶縁性樹脂(11)表面の改質された領域に金属原子を付着させるために、前記カルボキシル基の水素原子を金属原子に置き換えることを特徴とする請求項7記載の金属パターン形成方法。

【請求項9】 前記金属原子は銀であることを特徴とする請求項6記載の金属パターン形成方法。

【請求項10】 前記金属配線層(16)は、前記金属原子層(15)を電極とする電解メッキにより形成されることを特徴とする請求項6記載の金属パターン形成方法。

【請求項11】 前記絶縁性樹脂(16)表面の所望領域を改質する光線として、波長が180nm~250nmの

光線を使用することを特徴とする請求項6記載の金属パターン形成方法。

## 【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、金属パターン形成方法に関し、より詳しくは、薄膜多層回路基板などを構成するために絶縁性樹脂表面に配線を選択的に形成する金属パターン形成方法に関する。

【0002】

【従来の技術】近年、大型コンピュータなどに使用される回路基板においては、配線を高密度化するためにポリイミドなどの薄膜絶縁性樹脂層と配線層とを交互に積層して形成した薄膜多層回路基板が主流になっている。このような薄膜多層回路基板を構成するためには、たとえばシリコンウエハ上に薄膜絶縁性樹脂層を形成して層間の導通を取るためのビア孔を開け、その表面に選択的に配線パターンを形成し、その上に再び薄膜絶縁性樹脂層を形成してまた配線パターンを形成するというように、絶縁層と配線層の形成の工程を繰り返す。

【0003】従来、薄膜絶縁性樹脂表面に配線パターンを形成するためには、リフト・オフ法を用いる場合が多かった。配線パターンをリフトオフ法で形成するためには、例えば、まず絶縁性樹脂層上に感光性を有するレジストをスピンコートし、ベーキング後、配線パターンに対応するメタルマスクを介してレジストを露光・現像する。次にスパッタ法などによりレジスト上全面に配線金属を付着させる。その後、溶媒を使用して不用部分の配線金属をレジストと一緒に剥離して除去する。これにより、絶縁性樹脂層上に配線に必要な金属部分だけが残されて、配線パターンが形成される。

【0004】

【発明が解決しようとする課題】しかしながら、このような従来の配線の形成方法では、配線を形成するために多くの時間が必要であり、配線形成のスループットが低いという問題があった。たとえばリフトオフ法では、絶縁性樹脂層の上に配線パターンを形成するまでに、レジスト塗布、ベーキング、露光・現像、スパッタ、レジスト剥離など、レジストに関連する多くの工程を必要とする。

【0005】また、絶縁性樹脂層上に配線を選択的に形成するためにリフトオフ法を使用すると、いったんレジスト上全面に形成された配線金属層のうちの不用部分の配線金属が除去されるが、このとき不用な配線金属と一緒にレジストも除去されるので、除去された不要配線金属にレジストが混じって再利用することができず、配線金属材料が無駄になる。この配線金属の無駄により、結果的に薄膜多層回路基板のコストを上昇させるという問題が生じる。

【0006】本発明はこのような問題に鑑みてなされたものであって、絶縁性樹脂層表面に選択的に配線を形成

する金属パターン形成方法において、形成工程を簡略化してスループットを高めることを目的とする。

【0007】

【課題を解決するための手段】上記した課題は、図1に例示するように、絶縁性樹脂層1の表面に金属微粒子層2を形成する工程と、前記金属微粒子層2表面の所望領域にレーザを照射して、該所望領域にある前記金属微粒子層2を溶解する工程と、前記絶縁性樹脂層1表面から前記レーザの照射により溶解しなかった前記金属微粒子層2を除去する工程とを有することを特徴とする金属パターン形成方法により解決する。

【0008】前記金属微粒子層2は、金属微粒子と有機溶媒の混合物からなるペースト材料であり、前記金属微粒子層2は該ペースト材料をスキージングすることにより形成されることを特徴とする金属パターン形成方法により解決する。前記金属微粒子層2表面に前記レーザを照射する前に、前記金属微粒子層2を加熱して前記有機溶媒を取り除くことを特徴とする金属パターン形成方法によって解決する。

【0009】前記レーザは、不活性ガスの雰囲気中で照射されることを特徴とする金属パターン形成方法により解決する。前記レーザにより溶解しなかった前記金属微粒子層2は有機溶媒を用いて除去されることを特徴とする金属パターン形成方法により解決する。または、図2に例示するように、絶縁性樹脂11の表面の所望領域に所定エネルギーの光線を照射して、前記絶縁性樹脂11表面の所望領域を改質する工程と、前記絶縁性樹脂11表面の改質された領域に金属原子を付着させて、薄い金属原子層15を形成する工程と、前記金属原子層15を土台として金属配線層16を形成する工程とを有することを特徴とする金属パターン形成方法により解決する。

【0010】前記絶縁性樹脂11はポリイミド樹脂またはオレフィン樹脂であり、前記所定エネルギーの光線を照射することにより前記絶縁性樹脂11表面にカルボキシル基が生じることを特徴とする金属パターン形成方法により解決する。前記絶縁性樹脂11表面の改質された領域に金属原子を付着させるために、前記カルボキシル基の水素原子を金属原子に置き換えることを特徴とする金属パターン形成方法により解決する。

【0011】前記金属原子は銀であることを特徴とする金属パターン形成方法によって解決する。前記金属配線層16は、前記金属原子層15を電極とする電解メッキにより形成されることを特徴とする金属パターン形成方法により解決する。前記絶縁性樹脂16表面の所望領域を改質する光線として、波長が180nm～250nmの光線を使用することを特徴とする金属パターン形成方法により解決する。

【0012】

【作 用】本発明によれば、絶縁性樹脂層の表面に、金属微粒子を有機溶媒と混合したペースト状材料をスキ

ジングなどにより塗布して金属微粒子層を形成し、次にペースト状材料内の有機溶媒を加熱除去したあと、レーザを配線パターンのメタルマスクを介して絶縁性樹脂層表面の配線パターン形成領域に照射する。これにより、金属微粒子が溶解して一体となって絶縁性樹脂層表面に付着する。レーザ照射を不活性ガス雰囲気で行うと、金属微粒子を酸化させ変質させることなく溶解することができる。そして、絶縁性樹脂層表面の溶解しなかった不用の金属微粒子を、たとえば有機溶媒を使って除去する。これにより、絶縁性樹脂層表面にはレーザを照射した領域の金属層が残って配線パターンが形成される。

【0013】したがって、リフトオフ法などと比べて金属パターン形成方法を簡略化させることができる。また、絶縁性樹脂層表面から除去された不用の金属微粒子を再利用することができる。また別の方法として、ポリイミド樹脂やオレフィン樹脂などの絶縁性樹脂層の表面の配線パターン形成領域に、レーザなどの所定エネルギーの光線を配線パターンのメタルマスクを介して照射し、絶縁性樹脂層表面を金属原子が付着するように改質する。これは、所定エネルギーの光線の照射により樹脂中のベンゼン環が壊れて（開鎖して）、樹脂表面にたとえばカルボキシル基が生じるように改質される。次に絶縁性樹脂層表面の改質された領域に、たとえばトリフルオロ酢酸銀溶液により、Agなどの金属原子を単原子層に付着させて金属原子層を形成する。この金属原子層を電極として電解メッキをして、金属原子層の上に配線金属層を形成する。

【0014】これにより、リフトオフ法などと比べて金属パターン形成方法を簡略化させることができる。また、配線金属を絶縁性樹脂基板の配線形成領域だけに付着させることができるので、不用の配線金属を除去し廃棄するような無駄を回避することができる。

【0015】

【実施例】そこで、以下に本発明の実施例を図面に基づいて説明する。

（第1の実施例）図1(a)～図1(d)は、本発明の第1の実施例に係る金属パターン形成方法の各工程を概略的に示したものである。

【0016】図1(a)では、ポリイミド樹脂、オレフィン樹脂などからなる絶縁性樹脂薄膜1の上に、平均粒径約2μmのCu微粒子（銅微粒子）をアセトンなどの溶媒に混合したCu微粒子含有層2が厚さ10μmに形成されている。この絶縁性樹脂薄膜1は、実際には、図示されていないシリコンウエハなどの基板上に形成されているが、この図では省略してある。この絶縁性樹脂薄膜1を形成する基板は、セラミック、マイカ、ガラス、窒化アルミ（AlN）などの絶縁性基板、またはアルミニウムなどの導電性基板でもよい。また、Cu微粒子含有層2の金属微粒子の材料は、導電性が高くかつ融点が高い金属が好ましく、アルミニウムなどでもよい。Cu微粒

子含有層2は、Cu微粒子と溶媒を混合してペースト状にしたものを絶縁性樹脂薄膜1表面にスキージングすることにより、簡単に均一に塗布することができる。

【0017】次に図1(b)では、Cu微粒子含有層2を乾燥させる。この工程では、図1(a)に示したCu微粒子含有層2を形成した基板を、Cuが酸化しないような窒素雰囲気中のオープンに入れ、60℃で10分間乾燥する。これにより、Cu微粒子含有層2中の溶媒が蒸発してCu微粒子だけが残り、固まった状態のCu微粒子層3になる。

【0018】次に図1(c)に示すように、ステンレスよりなるメタルマスク4を介してエキシマレーザ5をCu微粒子層3表面に照射し、Cu微粒子層3内のCu微粒子を選択的に溶融させる。メタルマスク4は、絶縁性樹脂薄膜1上に形成する配線パターンが刻まれたものである。レーザ5は、波長248nmのKrFエキシマレーザを、エネルギー密度1.0J/cm<sup>2</sup>、照射時間150nsで10パルスで照射する。このとき、Cuが酸化しないように、雰囲気ガスとして不活性なアルゴンガスを使用する。

【0019】これにより、Cu微粒子層3のレーザ5が照射された領域は約1000℃の温度に上昇してCu微粒子がそれぞれ溶融して一体化し、溶融Cu領域3aとして絶縁性樹脂薄膜1表面に付着する。また、Cu微粒子層3のうちレーザ5が照射されなかった領域は溶融していないので、Cu微粒子がそれぞれ分離したばらばらの状態のままである。

【0020】最後に図1(d)では、Cu微粒子層3に選択的にレーザ照射した基板を、容器7内のアセトン、エタノールなどの有機溶媒6に浸して軽く攪拌する。この有機溶媒6としては、Cuなどの金属微粒子を酸化させないものが好ましい。これにより、Cu微粒子層3の溶融Cu領域3a以外のCu微粒子は、すべて絶縁性樹脂薄膜1表面から分離して有機溶媒6に混ざり、しばらくすると容器7の下の方に沈殿する。溶融Cu領域3aのCu微粒子は、溶融して絶縁性樹脂薄膜1表面に付着しているため、有機溶媒6中に離れ除去されることはない。

【0021】こうして、絶縁性樹脂薄膜1表面から溶融Cu領域3a以外の領域のCu微粒子が除去されると、結果的に、絶縁性樹脂薄膜1表面には溶融Cu領域3aが残され配線となる。本実施例では、幅10μm厚さ5μmの配線を形成した。このように、絶縁性樹脂薄膜表面にCu微粒子を有機溶媒と混合したペーストを塗布し、そのペースト層に配線パターンのメタルマスクを介して選択的にレーザを照射することにより、レーザ照射領域のCu微粒子が溶融して絶縁性樹脂薄膜表面に付着する。その後、この基板を有機溶媒中に浸すことにより、レーザ照射されなかった領域の不用のCu微粒子は有機溶媒中に分離し、絶縁性樹脂薄膜表面には溶融した

Cu層だけが残し、配線が形成される。

【0022】ここで形成された配線層の上に絶縁性樹脂薄膜を形成し、その上に以上で説明したような方法で配線を形成し、それを繰り返すことで、薄膜多層回路基板を形成することができる。したがって、リフトオフ法のような長い工程を必要としないので、配線形成が簡略化され、配線形成のスループットが向上する。

【0023】また、有機溶媒により絶縁性樹脂薄膜表面から分離した不用のCu微粒子は、有機溶媒から分離してまたは有機溶媒と混合された状態で再利用が可能であり、配線金属の無駄が大幅に減少し、薄膜多層回路基板の製造コストを削減することができる。

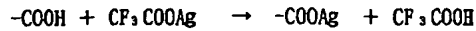
(第2の実施例) 図2(a)～(c)は、本発明の第2の実施例に係る配線形成方法の各工程を、概略的に示したものである。

【0024】図2(a)では、ポリイミド樹脂、オレフィン樹脂など絶縁性樹脂薄膜11の表面に、配線パターンが形成されたステンレスよりなるメタルマスク12を介してレーザ13を照射する。絶縁性樹脂薄膜11は、実際には、シリコンウェハなどの基板上に形成されているが、ここでは省略してある。また、この基板としては、セラミック、マイカ、ガラス、窒化アルミ(AIN)などの絶縁性基板、またはアルミニウムなどの導電性基板でもよい。レーザ13は、波長248nmのKrFエキシマレーザを使用し、エネルギー密度100mJ/cm<sup>2</sup>、照射時間15ns(1パルス)で、大気雰囲気中で照射される。このように、レーザ13を絶縁性樹脂薄膜11の配線パターン形成領域に照射することにより、絶縁性樹脂薄膜11表面のポリイミド樹脂やオレフィン樹脂などに含まれるベンゼン環が壊れて(開鎖して)、絶縁性樹脂薄膜11表面にカルボキシル基(-COOH)が生じる。この開鎖の深さは絶縁性樹脂薄膜11表面から3000オングストローム程度であり、カルボキシル基は絶縁性樹脂薄膜11の表面側に出るように生じる。このように、絶縁性樹脂薄膜11の表面が改質するためには、レーザ13の波長、照射時間、およびエネルギー密度の条件が適切でなければならない。波長は、絶縁性樹脂薄膜11に使用されている樹脂の吸収帯に含まれる必要があり、ここでは180nm～250nmの範囲が好ましく、具体的にはArFエキシマレーザ(波長193nm)がより好ましい。また、エネルギー密度が高すぎると絶縁性樹脂薄膜11が蒸発してしまうので、エネルギー密度は40mJ/cm<sup>2</sup>(閾値)～100mJ/cm<sup>2</sup>ある程度の高さに抑えた方がよい。照射時間は、レーザ13の波長とエネルギー密度に関係するエネルギー量で決まる。

【0025】図2(b)では、選択的にレーザ照射された絶縁性樹脂薄膜11を、アセトン10で洗浄後、10<sup>-2</sup>Mのトリフルオロ酢酸銀(CF<sub>3</sub>COOAg)溶液14に10分間浸漬する。これにより、下記のような化学反応が進み、絶縁性樹脂薄膜11表面側にあるカルボキシル基の水

素原子とトリフルオロ酢酸銀14のAg原子が置換し、絶縁性樹脂薄膜11表面にはAg原子の単原子層が形成される。

【0026】



Ag原子は、実際にはポリイミド樹脂やオレフィン樹脂を構成する有機化合物の一部として結合しているが、前述したように、カルボキシル基は絶縁性樹脂薄膜11の表面側に生じるので、Ag原子も絶縁性樹脂薄膜11の表面にだけ配列し、Ag原子層5が形成される。このカルボキシル基は、絶縁性樹脂薄膜11表面のレーザ13が照射された領域だけに生じるので、このAg原子層15はレーザ13が照射された領域だけに形成される。また明らかに、このAg原子層15は導電性を有する。

【0027】図2(c)では、配線パターンとして、絶縁性樹脂薄膜11表面のAg原子層15上にCu配線層16を形成する。これは、絶縁性樹脂薄膜11を硫酸銅溶液(図示せず)の中に入れ、Ag原子層15を電極として電解メッキを行い、Ag原子層15がある領域だけにCu配線層16を成長させることにより行われる。本実施例では、幅10μm、厚さ5μmのCu配線層16を形成した。

【0028】このように、絶縁性樹脂薄膜11の表面に、配線パターンのメタルマスク12を介して所定エネルギーを有するレーザ13を照射して、絶縁性樹脂薄膜11表面を選択的に改質する。そして、その改質された部分にトリフルオロ酢酸銀溶液によってAg原子層15を形成し、そのAg原子層15を電極として利用して電解メッキによりCu配線層16を形成することにより、絶縁性樹脂薄膜11上に配線パターンを形成することができ

【0029】したがって、配線パターンを形成する方法において、リフトオフ法によりも工程を簡略化することができるので、配線形成のスループットが向上する。また、絶縁性樹脂薄膜11表面の配線パターン形成領域だけに選択的に配線金属が付着されるので、配線金属の無駄がなくなり、配線形成のコストが削減される。また、この実施例において形成した配線パターンの上にさらに絶縁性樹脂薄膜を積層し、その上に同じ方法で配線パターンを形成する。これを繰り返すことにより、薄膜回路基板を容易に形成することができる。

(第3の実施例)次に、本発明の第3の実施例に係る配線形成方法を説明する。

【0030】本実施例は、先に説明した第2の実施例と原理的には同じであり、図2(a)～図2(c)で説明した工程と流れは同じである。第2の実施例と異なる点は、第2の実施例では2図(a)の工程において絶縁性樹脂薄膜11表面を選択的に改質するためエキシマレーザを使用した

【0031】水銀ランプによる波長185nmの紫外線は、エネルギー密度20mJ/cm<sup>2</sup>、照射時間100min、10<sup>-3</sup>Torr以下の減圧雰囲気中で照射される。水銀ランプを使用すると、レーザを使用する場合よりもエネルギー密度が低く照射時間が長くなるので、照射部分が周囲の酸素の影響を受けないように、雰囲気を真空にする必要がある。

【0032】絶縁性樹脂薄膜表面の所望領域を改質した後は、第2の実施例と同様に、改質された領域にトリフルオロ酢酸銀水溶液によりAg原子層を形成し、そのAg原子層の上に配線金属層を成長させて配線パターンを形成する。また本実施例においても、第2の実施例と同様の作用・効果が得られる。

【0033】

【発明の効果】以上述べたように本発明によれば、基板上に形成された絶縁性樹脂薄膜の上にCuなどの金属微粒子を含むペーストを塗布し、そのペースト層の配線パターンを形成する領域にレーザを照射すると、レーザ照射領域の金属微粒子が熔融して絶縁性樹脂薄膜表面に付着し、レーザ照射により熔融しなかった領域の金属微粒子は有機溶媒で除去される。これにより、リフトオフ法などと比べて、配線形成工程が簡略化され、配線形成のスループットを高めることができる。また、絶縁性樹脂薄膜表面から除去された不用品金属微粒子は、回収が容易で再利用することができるので、配線形成のコストを低減することができる。

【0034】また、本発明の別の方法によれば、基板上に形成された絶縁性樹脂薄膜表面の配線パターン形成領域に所定エネルギーの光線を照射して表面を改質し、その改質領域にごく薄い金属原子層を形成させ、この金属原子層を土台として配線金属層を形成する。これにより、この方法においても、リフトオフ法などと比べ、配線を形成するための工程が簡略化され、配線形成のスループットを高めることができる。さらに、配線を形成するために必要な金属材料だけが絶縁性樹脂薄膜表面に付着され、リフトオフ法のように配線金属材料が絶縁性樹脂薄膜表面から除去されて廃棄されることがないので、配線金属材料の無駄がなくなり配線形成のコストを低くすることができる。

【図面の簡単な説明】

【図1】本発明の第1の実施例に係る配線形成方法を示し、(a)～(d)はその各工程を示す図である。

【図2】本発明の第2の実施例に係る配線形成方法を示し、(a)～(c)はその各工程を示す図である。

【符号の説明】

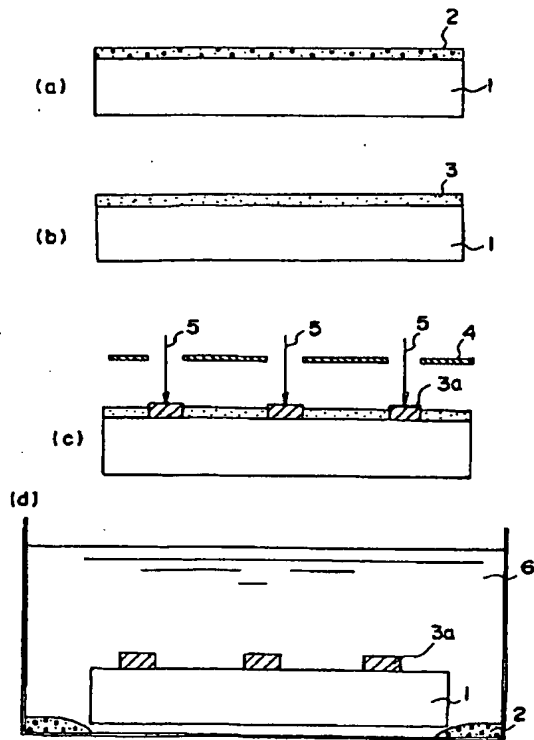
- 1、11 絶縁性樹脂薄膜
- 2 Cu微粒子含有層
- 3 Cu微粒子層
- 3a 熔融Cu層
- 4、12 メタルマスク



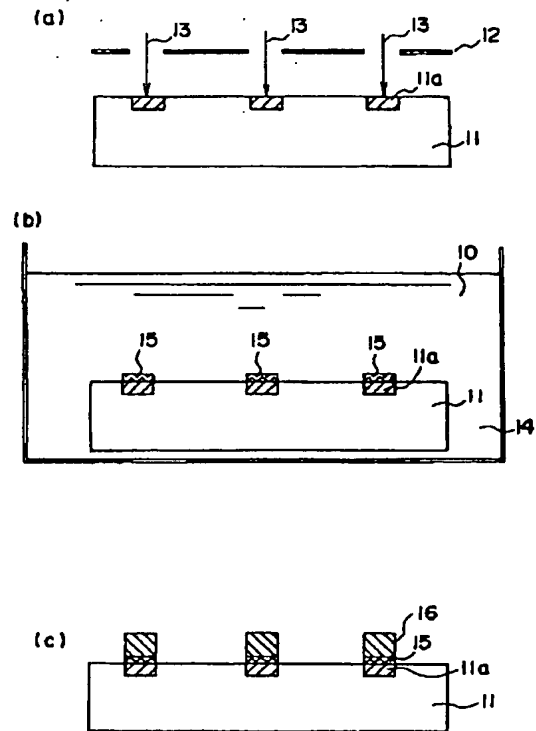
- 5、13 レーザ  
6 有機溶媒  
7 容器

- 14 トリフルオロ酢酸銀溶液  
15 Ag原子層  
16 Cu配線層

【図1】



【図2】



フロントページの続き

(51) Int. Cl. 6

H05K 3/46

識別記号

庁内整理番号

F 1

技術表示箇所

E 6921-4E